

# PATENT SPECIFICATION

(11) 1 429 494

1 429 494

- (21) Application No. 16140/73 (22) Filed 4 April 1973  
 (31) Convention Application No. 7 204 581  
 (32) Filed 6 April 1972  
 (31) Convention Application No. 7 217 257  
 (32) Filed 19 Dec. 1972 in  
 (33) Netherlands (NL)  
 (44) Complete Specification published 24 March 1976  
 (51) INT CL<sup>2</sup> C10G 13/08, 23/02  
 (52) Index at acceptance C5E 20 21H2  
 (72) Inventors PETER LADEUR and GERRIT VAN GOOSWILLIGEN



## (54) PROCESS FOR THE PREPARATION OF A LUBRICATING OIL

(71) We, SHELL INTERNATIONAL-  
 ALE RESEARCH MAATSCHAPPIJ  
 B.V., a company organised under the laws of  
 The Netherlands, of 30 Carel van Bylandtlaan,  
 The Hague, the Netherlands, do hereby  
 declare the invention, for which we pray that  
 a patent may be granted to us, and the method  
 by which it is to be performed, to be particu-  
 larly described in and by the following state-  
 ment:—

The invention concerns a process for the  
 preparation of a lubricating oil having a  
 dynamic viscosity at  $-17.8^{\circ}\text{C}$  of at most 24  
 P and a kinematic viscosity at  $98.9^{\circ}\text{C}$  of at  
 least 7.0 cS.

According to the SAE classification, lubri-  
 cating oils for internal combustion engines are  
 divided on the basis of their viscosity into two  
 groups which are designated by the names  
 winter grade and normal grade. Each of these  
 groups is subdivided into a number of classes.  
 Lubricating oils which are classed as winter  
 grade are designated by the letter W, preceded  
 by a numeral, for example an SAE 5 W,  
 SAE 10 W or SAE 20 W oil. These oils have  
 to satisfy a certain requirement as regards their  
 dynamic viscosity at  $-17.8^{\circ}\text{C}$ . Lubricating  
 oils classed as normal grade are designated  
 merely by a numeral, for example an SAE  
 20, SAE 30, SAE 40 or SAE 50 oil. These  
 oils must satisfy a certain requirement as  
 regards their kinematic viscosity at  $98.9^{\circ}\text{C}$ .  
 Lubricating oils which belong to only one SAE  
 class (either of the winter grade or of the  
 normal grade) are designated single-grade  
 lubricating oils. Examples of widely used  
 single-grade lubricating oils are SAE 20 and  
 SAE 30 oils. In addition to the single-grade  
 lubricating oils, lubricating oils are also known  
 which satisfy both the viscosity requirement  
 of a class of the winter grade and the viscosity  
 requirement of a class of the normal grade.  
 When used as motor oil these multigrade  
 lubricating oils have the advantage that in  
 winter they are sufficiently thin to cause no

difficulties in a cold start, and sufficiently thick  
 at the temperature of the running engine to  
 lubricate properly. An important class of  
 multigrade lubricating oil is the 10W/30 oils.

Multigrade lubricating oils in the 10W/30  
 class can be prepared by incorporating a  
 number of additives with quality-improving  
 properties into a base oil consisting of a  
 lubricating oil or a blend of lubricating oils  
 having a high viscosity index obtained in the  
 conventional manner or by hydrocracking,  
 which base oil in itself does not satisfy the  
 10W/30 specification.

The preparation of high viscosity index  
 lubricating oils in the conventional manner is  
 carried out as follows. A paraffinic petroleum  
 crude oil is separated by distillation at  
 atmospheric pressure into a number of distil-  
 late fractions (in particular successively into  
 one or more gasoline, kerosine and light gas  
 oil fractions) and a residue (known as long  
 residue). This long residue is then separated  
 by distillation at reduced pressure into a  
 number of distillate fractions (in particular  
 successively into one or more heavy gas oil,  
 spindle oil, light machine oil and medium  
 heavy machine oil fractions) and a residue  
 (known as short residue). From the lubricating  
 oil fractions obtained in the distillation at  
 reduced pressure, the corresponding lubricating  
 oils are prepared by refining. The refining of  
 the spindle oil fraction, light machine oil frac-  
 tion and medium heavy machine oil fraction  
 is effected by removing aromatics and wax  
 from these fractions. In refining the short  
 residue, asphalt is first of all removed from  
 the residue. From the deasphalted oil thus  
 obtained, aromatics and wax are subsequently  
 removed. The residual lubricating oil prepared  
 in this way is designated bright stock. The wax  
 obtained during refining of the various lubri-  
 cating oil fractions is designated distillate or  
 residual slack wax, depending on the type of  
 lubricating oil fraction from which it is  
 derived.

50  
55  
60  
65  
70  
75  
80  
85  
90

The lubricating oils prepared in the manner described above can be used, either as such or after blending, as base oils for the preparation of 10W/30 oils. The 10W/30 oils are prepared by incorporating into the base oils a number of additives with quality-improving properties. These additives may be divided into two groups. The first group comprises, among other additives, those to inhibit oxidation (anti-oxidants), corrosion (corrosion inhibitors), the formation of foam (anti-foaming agents) and deposits in the engine (detergents), as well as additives to improve the lubricating effect at high pressure (extreme pressure additives). The additives belonging to this group generally have a molecular weight which does not exceed a value of 10,000 and is generally far below this value. The lubricating oil additive packages marketed by a number of manufacturers are generally composed of additives of this type. The incorporation of such a lubricating oil additive package into a base oil has only a slight effect on the viscosity index of this oil, even if the additive package is used in a rather high concentration. Depending on the composition of the additive package which is incorporated into the oil, the viscosity index of the oil remains constant, increases somewhat, or even decreases slightly. Reference hereinafter to "additive package" means a blend of lubricating oil additives belonging to the above-mentioned first group; a property of this blend is that when it is incorporated into a base oil in a concentration of 15%, by weight, the viscosity index of this formulation (85%, by weight, of base oil + 15%, by weight, of blend) is not more than 10 units higher than the viscosity index of the base oil. The second group of additives having quality-improving properties used in the preparation of 10W/30 oils are the polymeric viscosity index improvers. The additives in this group generally have a molecular weight which exceeds a value of 10,000 and is frequently far in excess of this value.

The use of polymeric viscosity index improvers for the preparation of the present multigrade lubricating oils has serious drawbacks. In the first place, the high molecular weight compounds (generally polyalkyl acrylates and polyalkyl methacrylates) used for this purpose are insufficiently resistant to the shearing forces which occur in the engine and, moreover, are sensitive to oxidation. As a result, the polymers are decomposed in the engine and, in addition to fouling of the engine by decomposition products, a permanent decrease in the viscosity of the oil takes place. Furthermore, a temporary loss of viscosity occurs while the lubricating oil is being used, because the polymers become oriented under the influence of the shearing forces in the engine, which leads to reduced internal friction. As the shearing forces increase, the

apparent viscosity of the polymer-containing oil approaches that of the polymer-free oil.

It is clear from the above that there is an urgent need for lubricating oils which satisfy the 10W/30 specification without the addition of a polymeric viscosity index improver. Attempts to prepare such oils in the conventional manner, i.e. by distillation and refining, have not been successful.

It has now been found that lubricating oils which satisfy the 10W/30 specification either as such or after the addition of an "additive package," but without the addition of a polymeric viscosity index improver, can be prepared in good yield by catalytic hydrocracking of wax, provided that the following requirements regarding the wax starting material, the catalyst, the hydrocracking conditions and the working-up of the hydrocrackate are met.

The starting material is a wax of which more than 30%, by weight, boils above 520°C and which is obtained in the dewaxing of a residual mineral oil fraction.

The hydrocracking catalyst is a catalyst which contains nickel sulphide and/or cobalt sulphide and in addition molybdenum sulphide and/or tungsten sulphide and also fluorine, the catalyst carrier material being alumina.

The hydrocracking is carried out at a temperature between 325°C and 425°C and under such conditions that the resultant liquid reaction product consists of 25 to 95%, by weight, of components having a boiling point in excess of 400°C.

The working-up of the hydrocrackate is effected by separating it by distillation into one or more light fractions and a residual fraction having an initial boiling point between 350°C and 470°C and the desired lubricating oil is prepared from this residual fraction by dewaxing.

Lubricating oils prepared in this manner may satisfy the 10W/30 specification, either as such or after the addition of an additive package, but without the addition of a polymeric viscosity index improver; and they may be characterized as lubricating oils having a dynamic viscosity of at most 24 P at -17.8°C (measured according to ASTM standard D 2602/71) and a kinematic viscosity of at least 7.0, and preferably of at least 8.4 cS at 98.9°C (measured according to ASTM standard D 445/71).

According to the present invention a process for the preparation of a lubricating oil, comprises hydrocracking wax of which more than 30%, by weight, boils above 520°C and which is obtained by dewaxing a residual mineral oil fraction, said hydrocracking being effected at a temperature between 325°C and 425°C over a fluorine-containing sulphidic catalyst containing on alumina as carrier nickel and/or cobalt and molybdenum and/or tungsten so as to form a liquid reaction product, 25 to 95%, by weight, of which consists of com-

ponents having a boiling point in excess of 400°C, separating said reaction product by distillation into one or more light fractions and a residual fraction having an initial boiling point between 350°C and 470°C, and dewaxing the residual fraction to form a lubricating oil having a dynamic viscosity of at most 24 P at -17.8°C and a kinematic viscosity of at least 7.0 cS at 98.9°C.

For the avoidance of any doubt it is noted that references herein to "alumina" as carrier in the catalysts used in the process of the present invention include silica-aluminas.

The process of the present invention enables said lubricating oil product to be produced in a yield of at least 15%, by weight, based on the feed wax. The feed wax in the process of the invention is preferably a wax obtained in the dewaxing stage in the preparation of lubricating oil in a conventional manner. Before a residual lubricating oil fraction can be dewaxed, asphalt first has to be removed therefrom. Deasphalting can be carried out by treating the residual lubricating oil fraction with a low-boiling paraffinic hydrocarbon, such as ethane, propane, butane or pentane, propane being preferred. Aromatics and wax are subsequently removed from the deasphalted oil obtained in this way. The removal of aromatics from the deasphalted oil may be carried out by treating the deasphalted oil with a selective solvent for aromatic hydrocarbons, such as furfural, phenol, cresol, or Chlorex, furfural being preferred. Finally wax is removed from the resultant oil, which is known as bright stock waxy raffinate. Dewaxing of the oil may be carried out by cooling the oil in the presence of a solvent. Dewaxing is preferably carried out with a mixture of methyl ethyl ketone and toluene as solvent at a temperature between -10°C and -40°C and using a solvent-to-oil volume ratio between 1 to 1 and 10 to 1. The sequence in which the removal of aromatics and wax from the deasphalted oil takes place is in principle arbitrary, but in order to minimize the volume of oil which is cooled during dewaxing, the dewaxing should preferably be carried out after the aromatics have been removed from the deasphalted oil.

The feed wax to the process of the present invention preferably contains less than 35%w of oil. It is also preferred that the residual mineral oil fraction from which the feed wax is obtained by dewaxing, is an oil fraction which after dewaxing at -30°C has a viscosity index of at least 55, and in particular at least 70.

The preferred catalysts used in the process in accordance with the present invention are those which contain 0.025-0.8 gram atoms, and in particular 0.05-0.7 gram atoms, of nickel and/or cobalt and 0.05-0.5 gram atoms, and in particular 0.1-0.4 atoms, of

molybdenum and/or tungsten per 100 g of alumina. The atomic ratio between (a) nickel and/or cobalt and (b) molybdenum and/or tungsten is preferably between 0.1:1 and 2:1, and in particular between 0.2:1 and 1.6:1.

The metals may be incorporated by any method known in the art for the preparation of catalysts containing several components on a carrier, for example, by co-impregnation of alumina in one or more stages with an aqueous solution containing salts of the metals concerned. The catalysts are used in the sulphidic form. The catalysts may be sulphided by any method known in the art for the sulphidation of catalysts, for example, by contacting the catalyst with a mixture of hydrogen and hydrogen sulphide or with hydrogen and a sulphur-containing hydrocarbon oil, such as a sulphur-containing gas oil.

The incorporation of fluorine into the catalysts may in principle be carried out in two manners. Fluorine may be incorporated into the catalyst by impregnating the latter during or after the preparation with a suitable fluorine compound, such as ammonium fluoride. It is also possible to incorporate fluorine into the catalyst by in situ fluoridation of the catalyst in an early stage of the hydrocracking process for which the catalyst is used (for example during or after the start-up of the process). In situ fluoridation of the catalysts may be carried out by adding a suitable fluorine compound, such as o-fluoro-toluene or difluoroethane, to the gas and/or liquid stream which is passed over the catalyst. In a number of cases it may be preferred to incorporate at least part of the fluorine into the catalyst by in situ fluoridation. The quantity of fluorine contained in the present catalysts is preferably 0.5 to 7%, by weight. The catalysts which are used in the hydrocracking of the feed wax may also contain promoters such as boron and phosphorus.

In the preparation of lubricating oil by the hydrocracking of feed wax according to the invention, very favourable results are achieved by using one of the following catalysts.

(a) A catalyst prepared by the impregnation of alumina with a solution containing (a) one or more nickel and/or cobalt compounds, (b) one or more molybdenum and/or tungsten compounds, (c) phosphate ions and (d) peroxide ions, followed by drying and calcination of the impregnated alumina, fluorine being incorporated either during or after the impregnation and said catalyst being sulphided before use.

(b) A catalyst prepared by incorporating into an alumina hydrogel one or more nickel and/or cobalt compounds and one or more molybdenum and/or tungsten compounds in a sufficient concentration to impart a metal content, expressed as metal oxides, of 30 to

65%, by weight, to the finished catalyst followed by drying and calcination of the metals-containing hydrogel, fluorine being incorporated either during or after formation of said metals-containing hydrogel and said catalyst being sulphided before use, the alumina hydrogel into which the metal compounds are incorporated being a hydrogel which after drying and calcination yields a xerogel with a compacted bulk density of 0.75 to 1.6 g/ml and a pore volume of 0.15 to 0.5 ml/g.

(c) A catalyst prepared by treating a composition containing alumina, water, one or more water-soluble salts of nickel and/or cobalt and one or more water-soluble salts of molybdenum and/or tungsten, with a hydrogen sulphide-containing gas at a temperature below 150°C and subsequently heating the material in a hydrogen-containing gas to a final temperature in excess of 200°C, the quantity of water present in the composition which is treated with the hydrogen sulphide containing gas corresponding with the quantity of water present in the composition after drying in a dry gas at 110°C, increased by 20% to 120% of the quantity of water which the dried composition can absorb in the pores of the carrier at 20°C, fluorine being incorporated in said catalyst either during or after preparation thereof.

The catalysts which are used in the hydrocracking of the feed wax preferably contain as catalytically active metal components either nickel and molybdenum or nickel and tungsten.

Particularly suitable hydrocracking conditions for the process of the present invention are a pressure of 10 to 250 bar, a space velocity of 0.2 to 5 kg of feed per litre of catalyst per hour and a hydrogen/feed ratio of 100 to 5000 NI of hydrogen per kg of feed. The hydrocracking of the feed wax is preferably carried out under the following conditions: a temperature of 360°C to 415°C, a pressure of 25 to 200 bar, a space velocity of 0.5 to 1.5 kg of feed per litre of catalyst per hour and a hydrogen/feed ratio of 500 to 2500 NI per kg of feed.

Preferably, the liquid product from the hydrocracking stage comprises 40 to 70%, by weight, of components having a boiling point in excess of 400°C and the residual fraction has an initial boiling point between 390°C and 450°C.

To prepare a suitable lubricating oil from the residual fraction the latter is dewaxed. Dewaxing is preferably carried out by cooling the oil in the presence of a solvent. Very suitable for this purpose is a mixture of methyl ethyl ketone and toluene at a temperature between -10°C and -40°C and a solvent-to-oil volume ratio between 1 to 1 and 10 to 1. In order to increase the yield of desired lubricating oil, it is preferred to recycle to

the hydrocracking reactor at least a portion of the wax separated during dewaxing of the residual fraction.

The process according to the invention enables lubricating oils to be prepared which as such, i.e. without additives having been incorporated, meet the 10W/30 specification. The process according to the invention, moreover, enables lubricating oils to be prepared which as such do not meet the 10W/30 specification, but from which in a simple manner, without the use of polymeric viscosity index improvers, a 10W/30 oil can be prepared by incorporating a certain quantity of an additive package. The commercial additive packages which are at present used in practice in the preparation of multigrade lubricating oils comprise, for example, anti-oxidants, rust inhibitors, corrosion inhibitors, anti-wear agents, anti-foam agents, detergents, metal passivators and extreme-pressure additives.

In some cases, several quantity-improving properties are combined in a single additive. If the lubricating oils prepared according to the invention are intended for use as motor oils, it is advisable to incorporate an additive package, even if the lubricating oil as such meets the 10W/30 specification. In the preparation of 10W/30 oils according to the invention, it is preferred to incorporate such a quantity of the additive package into the base oil (which may or may not meet the 10W/30 specification) that an oil composition is obtained which comprises 87.5 to 95%, by weight, of base oil and 5% to 12.5%, by weight, of additives.

The invention is illustrated by the following Examples.

Eight catalysts (A—H) were used in hydrocracking experiments to prepare lubricating oil from six residual waxes (I—VI). The catalysts and feeds are described in more detail below.

**CATALYST A:** Ni/Mo/F/Al<sub>2</sub>O<sub>3</sub> catalyst with a pore volume of 0.44 ml/g and a specific surface area of 117.1 m<sup>2</sup>/g containing 6 parts, by weight, of nickel, 30 parts, by weight, of molybdenum and 7.5 parts, by weight, of fluorine per 100 parts, by weight, of alumina. This catalyst had been prepared by co-impregnation of alumina with an aqueous solution of ammonium molybdate, nickel nitrate and ammonium fluoride. After the degree of wetting had been set at 100%, the composition was first treated for 16 hours with H<sub>2</sub>S at 15 bar and 75°C, subsequently heated in 2 hours to 400°C in a stream of H<sub>2</sub>S-containing H<sub>2</sub> (9% by volume of H<sub>2</sub>S, 10 bar, 25000 NI.l<sup>-1</sup>.hour<sup>-1</sup>) and finally kept for approximately 2 hours in this gas stream. The expression "degree of wetting" relates to the quantity of water present in the composition in addition to the quantity of water which is present therein after drying of the composition in a dry gas at 110°C. The degree of wetting is

expressed as a percentage of the quantity of water which the dried composition can absorb in the pores of the carrier at 20°C.

**CATALYST B:** Ni/Mo/F/Al<sub>2</sub>O<sub>3</sub> catalyst with a pore volume of 0.23 ml/g and a specific surface area of 63.0 m<sup>2</sup>/g containing 6 parts, by weight, of nickel, 30 parts, by weight, of molybdenum and 7.5 parts, by weight, of fluorine per 100 parts by weight of alumina. This catalyst was prepared in the same way as catalyst A with the exception that in the present case another type of alumina was used.

**CATALYST C:** Ni/W/F/Al<sub>2</sub>O<sub>3</sub> containing 5 parts, by weight, of nickel, 38 parts, by weight, of tungsten per 100 parts, by weight, of alumina and 2.4%, by weight, of fluorine. This catalyst was prepared in the same manner as catalysts A and B, with the exception that in the present case a fluorine-free impregnation liquid was used which contained ammonium tungstate and nickel nitrate and that fluorine was incorporated into the catalyst by fluorination in situ.

**CATALYST D:** Ni/Mo/P/F/Al<sub>2</sub>O<sub>3</sub> catalyst containing 4.2 parts, by weight, of nickel, 17.7 parts, by weight, of molybdenum and 3.1 parts, by weight, of phosphorus per 100 parts by weight of alumina and 1.6%, by weight, of fluorine. This catalyst had been prepared by co-impregnation of alumina with an aqueous solution containing nickel nitrate, phosphoric acid, ammonium molybdate and hydrogen peroxide, and subsequent drying and calcination of the composition. Fluorine was incorporated into the catalyst by fluorination in situ.

**CATALYST E:** Ni/W/F/Al<sub>2</sub>O<sub>3</sub> catalyst containing 31 parts, by weight, of nickel, 58 parts, by weight, of tungsten and 7.5 parts, by weight, of fluorine per 100 parts, by weight, of alumina.

**CATALYST F:** Ni/W/F/Al<sub>2</sub>O<sub>3</sub> catalyst containing 31 parts, by weight, of nickel and 58 parts, by weight, of tungsten per 100 parts, by weight, of alumina and 6%, by weight, of fluorine.

**CATALYST G:** Ni/W/F/Al<sub>2</sub>O<sub>3</sub> catalyst containing 37 parts, by weight, of nickel and 70 parts, by weight, of tungsten per 100 parts, by weight, of alumina and 4.3%, by weight, of fluorine.

The catalysts E, F and G were prepared by mixing an alumina hydrogel with an aqueous solution containing nickel nitrate, ammonium tungstate and ammonium fluoride, the pH of which solution had been brought to 6.5 with the aid of 25% of ammonia. The mixture was heated to 80°C; the gel was filtered, extruded,

dried and calcined. After drying and calcination, the alumina hydrogel used in the preparation of these catalysts yielded a xerogel with a compacted bulk density between 0.75 and 1.6 g/ml and a pore volume between 0.15 and 0.5 ml/g.

**CATALYST H:** Ni/W/F/Al<sub>2</sub>O<sub>3</sub> catalyst containing 10 parts, by weight, of nickel and 60 parts, by weight, of tungsten per 100 parts, by weight, of alumina and 4.5%, by weight, of fluorine. This catalyst was prepared by co-impregnation of alumina with an aqueous solution containing nickel nitrate and ammonium tungstate and subsequent drying and calcination. Fluorine was incorporated into the catalyst by fluorination in-situ.

In situ fluorination of the catalysts C, D and H was carried out by adding o-fluorotoluene to the feed during the initial stage of the hydrocracking process.

#### FEED I (Bright stock slack wax)

Wax obtained in dewaxing a residual lubricating oil fraction (1) which had previously been deasphalted with propane and extracted with furfural. Initial boiling point of the wax: 520°C. Oil content of the wax 19.7%, by weight. The VI of the oil obtained by deoiling the wax was 97. Sulphur content of the wax: 0.34%, by weight.

#### FEED II (DAO slack wax)

Wax obtained in dewaxing a residual lubricating oil fraction (1) which had previously been deasphalted with propane. Initial boiling point of the wax: 520°C. Oil content of the wax: 9.8%, by weight. VI of the oil obtained by deoiling the wax: 78. Sulphur content of the wax: 0.85%, by weight.

#### FEED III (Bright stock slack wax)

Wax obtained in dewaxing a residual lubricating oil fraction (1) which had previously been deasphalted with propane and extracted with furfural. Initial boiling point of the wax: 520°C. Oil content of the wax: 21.1%, by weight. VI of the oil obtained by deoiling the wax: 98. Sulphur content of the wax: 0.66%, by weight.

#### FEED IX (Wax from hydrocracked bright stock slack wax)

Wax obtained by dewaxing a residual fraction of a hydrocrackate which had been prepared by hydrocracking of wax obtained by dewaxing a residual lubricating oil fraction (1) which had previously been deasphalted with propane and extracted with furfural. Initial boiling point of the feed wax: 390°C. Of this wax 92.5%, by weight boiled above 520°C. Oil content of the feed wax: 6%, by weight. VI of the oil obtained after the feed wax had been deoiled: 149. Sulphur content of the feed wax: 20 ppmw.

- FEED V** (Wax from hydrocracked bright stock slack wax)
- Wax obtained by dewaxing a residual fraction of a hydrocrackate which had been prepared by hydrocracking of wax obtained by dewaxing a residual lubricating oil fraction (1) which had previously been deasphalted with propane and extracted with furfural. Initial boiling point of the feed: 520°C. Oil content of the feed wax: 7%, by weight. VI of the oil obtained by de-oiling the feed wax: 150. Sulphur content of the feed wax: 20 ppmw.
- FEED VI** (Wax from mildly hydrocracked DAO)
- Wax obtained by dewaxing a residual fraction of a hydrocrackate which had been prepared by mild hydrocracking (hydrocracking conditions such that 25%, by weight, of the hydrocrackate boiled below the initial boiling point of the DAO feed) of a residual lubricating oil fraction (1) which had previously been deasphalted with propane. Initial boiling point of the feed wax: 520°C. Oil content of the feed wax: 21%, by weight. VI of the oil obtained by de-oiling the feed: 95. Sulphur content of the feed wax: 500 ppmw.
- The six residual lubricating oil fractions (1) from which the feed waxes I—VI were prepared had been obtained as residue in the distillation under reduced pressure of atmospheric distillation residues of paraffinic crude oils. Dewaxing was carried out by cooling the oils to a temperature of  $-30^{\circ}\text{C}$  in the presence of a 1:1 mixture of methyl ethyl ketone and toluene.
- The viscosity indices referred to herein were determined by ASTM standard D 2270. The hydrocracking experiments 1—26 were carried out under the following conditions:
- pressure: 150 bar, except for experiment 7; this experiment was carried out at a pressure of 50 bar.  
 temperature:  $375\text{--}410^{\circ}\text{C}$ .  
 space velocity:  $1\text{--}1.1\text{ hour}^{-1}$ .  
 hydrogen/feed ratio:  $2000\text{ Nl.l}^{-1}$ .  
 volume of catalyst bed: 100 ml.
- The catalysts were used in the sulphidic form. Sulphidation of the catalysts D—H was carried out by contacting them with hydrogen and a sulphur-containing gas oil. During hydrocracking of feeds IV—IV, butylmercaptan was added to these feeds in an amount sufficient to increase the total sulphur content of these feeds to 2500 ppmw. Residual fractions having an initial boiling point between  $365^{\circ}\text{C}$  and  $440^{\circ}\text{C}$  were separated from the hydrocracked products by distillation. From the residual fractions the corresponding lubricating oils were prepared by dewaxing the fractions. Dewaxing was carried out by cooling the oil to a temperature of  $-30^{\circ}\text{C}$  in the presence of a 1:1 mixture of methyl ethyl ketone and toluene.

The results of hydrocracking experiments 1-26 are shown in Table A.

TABLE A

Exp. No.	Cat. No.	feed No.	hydro-cracking temp., °C	quantity of material boiling above 400°C present in the liquid reaction product, %w	initial boiling point of the residual lub. oil fraction separated, °C	properties of the dewaxed residual lubricating oil fraction			
						yield based on feed, %w	kinematic viscosity at 98.9°C, cS	VI	Dynamic viscosity at -17.8°C, P
1	G	III	390	70	400	43	9.8	144	22.5
2	F	III	390	67	400	33	9.9	142	24
3	D	I	394	67	400	27	9.7	142	23
4	B	I	405	72	400	35	9.7	146	21.5
5	A	I	402	71	400	36	9.7	143	23.5
6	C	II	398	70	400	27	9.7	154	17
7	E	II	394	69	400	28	9.7	143	23.5
8	B	I	405	72	400	35	9.8	146	20
9	D	III	397	67	420	26	9.7	144	21
10	G	IV	375	86	390	30	10.0	154	18
11	G	V	375	88	390	28	9.9	155	18
12	A	I	410	60	400	37	8.7	143	18
13	A	I	395	77	365	37	9.3	143	22
14	A	I	400	72	385	38	9.4	142	21
15	A	I	405	65	410	37	9.4	145	20
16	A	I	410	44	440	26	9.4	144	21
17	B	I	405	72	390	36	9.4	146	19
18	D	III	397	67	400	27	8.9	145	17.5
19	D	III	397	67	405	27	9.1	145	18
20	D	III	397	67	410	27	9.3	145	19
21	G	IV	380	83	390	41	8.9	154	14
22	G	V	380	83	390	41	9.2	156	15
23	H	VI	385	56	400	40	8.5	149	16
24	G	III	400	46	400	31	8.6	148	16
25	F	I	390	63	400	38	8.6	146	17
26	A	II	410	72	400	35	8.4	149	15

- The experiments 1—26 shown in Table A are all hydrocracking experiments according to the invention. These experiments yielded at least 26%, by weight, based on the feed, of a lubricating oil having a dynamic viscosity of at most 24 P at  $-17.8^{\circ}\text{C}$  and a kinematic viscosity of at least 7.0 sS at  $98.9^{\circ}\text{C}$ . The lubricating oils prepared according to experiments 1—11 meet the 10W/30 specification (dynamic viscosity at  $-17.8^{\circ}\text{C}$  at least 12 P and at most 24P and kinematic viscosity at  $98.9^{\circ}\text{C}$  at least 9.6 cSt and at most 12.9 cS) as such, i.e. without the incorporation of additives.
- An additive package was incorporated into the lubricating oils prepared according to experiments 12—23 which do not meet the 10W/30 specification and into the lubricating oils prepared according to the experiments 8—11 which do meet the 10W/30 specification. Two additive packages were used, designated additive package A and additive package B. These additive packages differ as regards the chemical composition of the additives which they contain, but both have substantially the same effects, namely anti-oxidation, rust inhibition, wear resistance, corrosion inhibition, foam inhibition, metal passivation, improvement of the lubricating effect at high pressure and inhibition of deposits in the engine. Incorporation of additive package A into the lubricating oil yields a lubricating oil composition containing 92.5%, by weight, of the base oil and 7.5%, by weight, of the additive package. Incorporation of additive package B into the lubricating oil yields a lubricating oil composition containing 89.9%, by weight, of the base oil and 10.1%, by weight, of the additive package. The properties of the oil compositions prepared are shown in Table B.



TABLE B

base oil prepared according to exp. No.	properties of the base oil without additive package			properties of a composition comprising 92.5 %w of the base oil and 7.5 %w of the additive package A			properties of a composition comprising 89.9 %w of the base oil and 10.1 %w of the additive package B		
	VI	kinematic viscosity at 98.9°C, cS	dynamic viscosity at -17.8°C, P	VI	kinematic viscosity at 98.9°C, cS	dynamic viscosity at -17.8°C, P	VI	kinematic viscosity at 98.9°C, cS	dynamic viscosity at -17.8°C, P
12	143	8.7	18				143	9.8	22
13	143	9.3	22	140	9.9	24			
14	142	9.4	21	139	10.0	23			
15	145	9.4	20	142	10.0	22			
16	144	9.4	21	141	10.0	23			
17	146	9.4	19	143	10.0	21	147	10.3	23
18	145	8.9	17.5				145	9.9	21
19	145	9.1	18	143	9.7	21	145	10.1	22
20	145	9.3	19	143	9.9	21.5	145	10.4	23
21	154	8.9	14				156	9.9	18
22	156	9.2	15	155	9.8	17.5	154	10.3	19
23	149	8.5	16				149	9.6	20
8	146	9.8	20				147	10.9	24
9	144	9.7	21	144	10.4	22.5			
10	154	10.0	18	142	10.4	23.5			
11	155	9.9	18	156	10.6	20.5	157	11.1	22
				155	10.6	21	154	11.0	22

The results given in Table B show that lubricating oils prepared according to the invention which as such do not meet the 10W/30 specification (compare experiments 12—23) may be formulated to 10W/30 oils in a simple manner, without the addition of the customary polymeric viscosity improvers, by the incorporation of the additive package A or B. Incorporation of these additive packages into a lubricating oil prepared according to the invention which as such meets the 10W/30 specification (compare experiments 8—11) yields a 10W/30 oil of better quality.

In the process according to the invention it is essential for a fluorine-containing sulphidic catalyst to be used which contains nickel and/or cobalt and in addition molybdenum and/or tungsten on alumina as carrier. Two hydrocracking experiments were carried out

for comparison. In the first experiment a fluorine-free catalyst based on alumina was used and in the second experiment a fluorine-containing catalyst based on silica-alumina. The two experiments are described in more detail below.

#### COMPARATIVE EXPERIMENT 1.

A Ni/Mo/P/Al<sub>2</sub>O<sub>3</sub> catalyst containing 4.2 parts, by weight, of nickel, 17.7 parts, by weight, of molybdenum and 3.1 parts, by weight, of phosphorus per 100 parts, by weight, of alumina (catalyst D without fluorine), was used for the hydrocracking of feed I under the same conditions as those used in experiment 3, with the exception that in the present case the hydrocracking temperature was 445°C. The lubricating oil was worked up in the same manner as in experiment 3. Table C gives the results of comparison experiment 1 and those of experiment 3.

TABLE C

Experiment	hydrocracking temp., °C	yield based on feed, %w	VI	properties of the dewaxed residual lubricating oil fraction	
				kinematic viscosity at 98.9°C, cS	dynamic viscosity at -17.8° P
comparison experiment 1	445	12	140	9.1	22
experiment 3	394	27	142	9.7	23

The results shown in Table C demonstrate the unsuitability of the fluorine-free catalyst for the present purpose. At a hydrocracking temperature of 394°C the fluorine-containing catalyst gives a lubricating oil yield of 27%, by weight; at a hydrocracking temperature of 445°C (which is outside the scope of the present invention), the fluorine-free catalyst gives a lubricating oil yield of only 12%, by weight.

#### COMPARATIVE EXPERIMENT 2.

A Ni/W/F/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst containing 9%, by weight, of nickel, 17%, by weight, of tungsten and 2.5%, by weight, of fluorine on a carrier which comprised 26%, by weight, of alumina, the remainder being silica, was used for the hydrocracking of wax obtained in dewaxing a residual lubricating oil fraction de-asphalted with propane (VI of the de-asphalted oil after dewaxing at -19°C: 77). The residual lubricating oil fraction from which the wax (DAO slack wax) was prepared had been obtained in the distillation under reduced pressure of an atmospheric distillation residue of a North African crude oil. Dewaxing was carried out by cooling the

oil to a temperature of -27°C in the presence of a 1:1 mixture of methyl ethyl ketone and toluene. Hydrocracking of the wax took place with the use of the catalyst in the sulphidic form at a temperature of 350°C, a pressure of 50 bar, a space velocity of 1 kg.l<sup>-1</sup>.hour<sup>-1</sup> and a hydrogen/feed ratio of 150 Nl/kg of oil. A residual fraction with an initial boiling point of 400°C was separated from the hydrocracked product by distillation and dewaxed by cooling the oil at a temperature of 27°C in the presence of a 1:1 mixture of methyl ethyl ketone and toluene. Thus, a dewaxed residual lubricating oil fraction was obtained in a yield of 20% by weight, based on feed, having a VI of 100, a kinematic viscosity at 98.9°C of 16.9 cS and a dynamic viscosity at -17.8°C in excess of 200 P.

The results of this experiment demonstrate the unsuitability of a silica-alumina based catalyst for the present purpose. The viscosity of the resultant lubricating oil is outside the limits for a 10W/30 oil at both temperatures and it is impossible to prepare a 10W/30 oil from the lubricating oil by incorporating an additive package.

## WHAT WE CLAIM IS:—

1. A process for the preparation of a lubricating oil which comprises hydrocracking wax of which more than 30%, by weight, boils above 520°C and which is obtained by dewaxing a residual mineral oil fraction, said hydrocracking being effected at a temperature between 325°C and 425°C over a fluorine-containing sulphidic catalyst containing on alumina as carrier nickel and/or cobalt and molybdenum and/or tungsten so as to form a liquid reaction product, 25 to 95%, by weight, of which consists of components having a boiling point in excess of 400°C, separating said reaction product by distillation into one or more light fractions and a residual fraction having an initial boiling point between 350°C and 470°C, and dewaxing the residual fraction to form a lubricating oil having a dynamic viscosity of at most 24 P at -17.8°C and a kinematic viscosity of at least 7.0 cS at 98.9°C.
2. A process as claimed in claim 1, in which said wax is a wax obtained as by-product in the preparation of lubricating oil in a conventional manner.
3. A process as claimed in claim 1, in which said wax is a wax obtained by dewaxing a deasphalted residual lubricating oil fraction.
4. A process as claimed in claim 3, in which said deasphalted residual lubricating oil fraction has had aromatics removed therefrom.
5. A process as claimed in any one of claims 1—4, in which said wax contains less than 35%, by weight, of oil.
6. A process as claimed in any one of claims 1—5, in which the catalyst which is used in the hydrocracking of the feed wax, contains 0.025 to 0.8 gram atoms of nickel and/or cobalt and 0.05 to 0.5 gram atoms of molybdenum and/or tungsten per 100 g of alumina.
7. A process as claimed in any one of claims 1—6, in which the catalyst which is used in the hydrocracking of the feed wax has an atomic ratio between (a) nickel and/or cobalt and (b) molybdenum and/or tungsten which is between 0.1:1 and 2:1.
8. A process as claimed in any one of claims 1—7, in which at least part of the fluorine has been incorporated into said catalyst by *in situ* fluoridation.
9. A process as claimed in any one of claims 1—8, in which said catalyst contains 0.5 to 7%, by weight, of fluorine.
10. A process as claimed in any one of claims 1—9, in which said catalyst is a catalyst prepared by impregnating alumina with a solution containing (a) one or more nickel and/or cobalt compounds, (b) one or more molybdenum and/or tungsten compounds, (c) phosphate ions and (d) peroxide ions, followed by drying and calcination of the impregnated alumina, fluorine being incorporated either during or after the impregnation and said catalyst being sulphided before use.
11. A process as claimed in any one of claims 1—9, in which said catalyst is a catalyst prepared by incorporating into an alumina hydrogel one or more nickel and/or cobalt compounds and one or more molybdenum and/or tungsten compounds in a concentration sufficient to impart a metal content, expressed as metal oxides, of 30% to 65%, by weight, to the finished catalyst, followed by drying and calcination of the metals-containing hydrogel, fluorine being incorporated either during or after formation of said metals-containing hydrogel and said catalyst being sulphided before use, the alumina hydrogel into which the metal compounds are incorporated being a hydrogel which after drying and calcination yields a xerogel having a compacted bulk density of 0.75 to 1.6 g/ml and a pore volume of 0.15 to 0.5 ml/g.
12. A process as claimed in any one of claims 1—9, in which said catalyst is a catalyst prepared by treating a composition containing alumina, water, one or more water-soluble salts of nickel and/or cobalt and one or more water-soluble salts of molybdenum and/or tungsten, with a hydrogen sulphide-containing gas at a temperature below 150°C and subsequently heating the material in a hydrogen-containing gas to a final temperature in excess of 200°C, the quantity of water present in the composition which is treated with the hydrogen sulphide-containing gas corresponding with the quantity of water present in the composition after drying in a dry gas 110°C increased by 20% to 120% of the quantity of water which the dried composition can absorb in the pores of the carrier at 20°C, fluorine being incorporated in said catalyst either during or after preparation thereof.
13. A process as claimed in any one of claims 1—12, in which the hydrocracking of the feed wax is carried out under the following conditions: a pressure from 10 to 250 bar, a space velocity of 0.2 to 5 kg of feed per litre of catalyst per hour and a hydrogen/feed ratio of 100 to 5000 NI of hydrogen per kg of feed.
14. A process as claimed in claim 13, in which the hydrocracking of the feed wax is carried out under the following conditions: a temperature of 360 to 415°C, a pressure of 25 to 200 bar, a space velocity of 0.5 to 1.5 kg of feed per litre of catalyst per hour and a hydrogen/feed ratio of 500 to 2500 NI of hydrogen per kg of feed.
15. A process as claimed in any one of claims 1—14, in which 40% to 70%, by weight, of the liquid product of the hydrocracking comprises components having a boiling point in excess of 400°C, and in which the initial boiling point of the residual fraction separated therefrom is between 390°C and 450°C.
16. A process as claimed in any one of claims 1—15, in which the dewaxing of said residual

- fraction is carried out by cooling it to a temperature between  $-10$  and  $-40^{\circ}\text{C}$  in the presence of a mixture of methyl ethyl ketone and toluene as solvent, the solvent-to-residual fraction ratio being between 1 to 1 and 10 to 1.
- 5 17. A process as claimed in any one of claims 1—16, in which wax separated during the dewaxing of said residual fraction is recycled to the hydrocracking step.
- 10 18. A process as claimed in any one of claims 1—17, in which the lubricating oil product has a kinematic viscosity of at least 8.4 cS at  $98.9^{\circ}\text{C}$ .
- 15 19. A process as claimed in any one of claims 1—18, which comprises incorporating in the lubricating oil product a conventional additive package containing no polymeric viscosity-index improver(s).
- 20 20. A process as claimed in claim 19, in which 5% to 12.5%, by weight, of said additive package is incorporated.
- 25 21. A process for the preparation of a lubricating oil having a dynamic viscosity of at most 24 P at  $-17.8^{\circ}\text{C}$  and a kinematic viscosity of at least 7.0 cS at  $98.9^{\circ}\text{C}$ , substantially as described hereinbefore and with particular reference to any one of experiments 1—26 of the examples.
- 30 22. A lubricating oil prepared by the process claimed in any one of claims 1—21.

ROY C. ROGERS,  
Chartered Patent Agent,  
Shell Centre,  
London SE1 7NA.  
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.